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SOME PHOSPHINE-SUBSTITUTED DERIVATIVES OF CARBOXYLATO RHODIUM CARBONYL COMPLEXES

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SUMMARY

The complexes $Rh_2(CO)_3(PPh_3)(OOCR)_2$ (R = Me, Et) have been prepared from the corresponding dinuclear carboxylato rhodium carbonyls by treatment with a controlled amount of triphenylphosphine. Both the substituted and unsubstituted dinuclear complexes are converted by an excess of the ligand into the mononuclear $Rh(CO)(PPh_3)_2(OOCR)$.

INTRODUCTION

The dinuclear carboxylato rhodium carbonyl complexes $[Rh(CO)_2(OOCR)]_2$, prepared first by Lawson and Wilkinson[1], have received relatively little attention. Recently we observed these complexes in the samples taken from hydroformylation experiments performed in the presence of $Rh_4(CO)_{12}$ as catalyst[2]. Since according to some patents[3] $Rh(CO)(PR_3)_2(OOCR')$ complexes are useful hydroformylating catalysts, the reaction between the dinuclear carboxylato complexes and phosphines seemed worthy of investigation.

RESULTS AND DISCUSSION

By proper adjustment of reaction conditions we were able to prepare monosubstituted dinuclear triphenylphosphine complexes of type (I):

$$[Rh(CO)_2(OOCR)]_2 \underset{CO}{\overset{PPh_3}{\rightleftharpoons}} \underset{(I)}{Rh_2(CO)_3(PPh_3)(OOCR)_2} \qquad (1)$$

(Ia) R = Me
(Ib) R = Et

Complexes (I) are the first known monosubstituted bridged dinuclear rhodium carbonyl derivatives. They are air-stable powders, dark brown in the mass but violet in a thin layer, moderately soluble in hexane and well soluble in benzene. The infrared spectra of the hexane solutions show three sharp and intense bands characteristic for the carbonyl ligands at 2075 (5.4), 2005 (10) and 1988 (2.4) cm^{-1} (relative intensities in parentheses). In KBr two further strong absorption bands appear at 1580 and

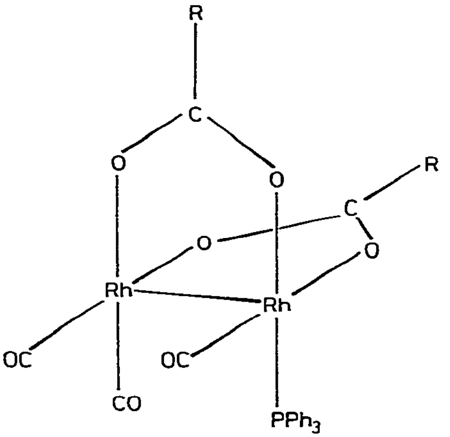


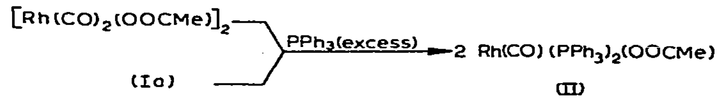
Fig. 1. Proposed structure of the monosubstituted carboxylatorhodium carbonyl complex.

1440 cm^{-1}, and can be assigned to the carboxyl groups. Based on analytical and IR data we propose the structure represented in Fig. 1.

Reaction (1) is reversible even at low p(CO): treatment of a 10^{-3} M solution of (Ib) at 25° with 1 atm of CO, converts about 50% of the complex into $[Rh(CO)_2(OOCEt)]_2$.

The formation of the complexes (I) shows, that the substitution reactions of $[Rh(CO)_2(X)]_2$ type complexes (X = halogen, OOCR, SR^4), which lead to the mononuclear $Rh(CO)(L)_2(X)$[5] and $Rh(CO)_2(L)(X)$[6], or, as found more recently, to the dinuclear $Rh_2(CO)_2(L)_2(X)_2$[7] derivatives, probably involve the bridged monosubstituted complexes $Rh_2(CO)_3(L)(X)_2$ as intermediates. To investigate this question further, the reactions of $[Rh(CO)_2(Cl)]_2$ with PPh_3, PBu_3 and $AsPh_3$, and $[Rh(CO)_2(OOCMe)]_2$ with PEt_3, PBu_3 and $AsPh_3$ were also studied in hexane solution by infrared spectroscopy. On the basis of the experience obtained in the preparation of complexes (I), solutions of the ligands were used and the L/Rh ratio was increased stepwise with IR monitoring. All the systems showed rather complex IR spectra in the 2100–1950 cm^{-1} region at L/Rh ratios between 0.2/1 and 1.5/1 pointing to several intermediates of the substitution reactions. In the case of $[Rh(CO)_2(OOCMe)]_2$, the new absorption bands could be assigned to $Rh_2(CO)_3(L)(OOCMe)_2$ complexes, but none of the systems was found to be suitable for isolation of these intermediates. With $[Rh(CO)_2(Cl)]_2$ the reactions appear to be even more complex, and the observed IR spectra of the reaction mixtures obtained under our conditions seem to agree only to a limited extent with published data[5-7]. Attempts to isolate pure compounds failed.

With excess triphenylphosphine, both complex (Ia) and $[Rh(CO)_2(OOCMe)]_2$ could be rapidly transformed into the disubstituted, mononuclear complex (II) in one step:



$$\left.\begin{array}{l}[Rh(CO)_2(OOCMe)]_2\\ (Ia)\end{array}\right\} \xrightarrow{PPh_3(excess)} \underset{(II)}{2\ Rh(CO)(PPh_3)_2(OOCMe)}$$

The yellow crystalline complex (II) is stable in air in the solid state. It is insoluble in hexane and slightly soluble in benzene. Its infrared spectrum in a nujol mull shows one band at 1980 cm^{-1}, characteristic of the carbonyl ligand and two bands at 1610 and 1470 cm^{-1} belonging to the carboxyl group. These values indicate that the Rh atom in (II) is probably pentacoordinated, with the carboxyl group functioning as a bidentate ligand.

EXPERIMENTAL

All preparations were performed under Ar.

Preparation of (Ia)

To 40 mg $[Rh(CO)_2(OOCMe)]_2$ in 50 ml hexane (the starting compound does not dissolve completely in this quantity of solvent, and this ensures a saturated solution), a hexane solution of PPh_3 (about 0.1 *M*) was added dropwise and the reaction mixture was repeatedly examined by IR spectroscopy. During the addition of PPh_3 the solid $[Rh(CO)_2(OOCMe)]_2$ completely dissolved, the colour of the solution changed from yellow to orange, and later the complex (Ia) separated as a dark brown powder. The addition of PPh_3 solution was continued until the IR spectrum of the solution showed the presence of only (Ia) (about 1 ml). Yield 45 mg (70%). (Found: C, 45.6; H, 3.5; Rh, 31.7. $C_{25}H_{21}O_7PRh_2$ calcd.: C, 44.8; H, 3.15; Rh, 30.8%.)

Preparation of (Ib)

(Ib) was prepared in a similar manner from the corresponding propionato complex. (Found: Rh, 29.9; P, 5.4. Mol.wt., 730±30. $C_{27}H_{25}O_7PRh_2$ calcd.: Rh, 29.5; P, 4.45%. Mol.wt., 698.) (Ib) was analysed by Karl Fischer titration [$P^{III}+Rh^{I}$ content[8,9]] too. Karl Fischer percentage[8]: found: 7.7, calcd.: 7.72%.

Preparation of (II)

$[Rh(CO)_2(OOCMe)]_2$ (60 mg) was dissolved in 100 ml hexane and 300 mg PPh_3 in 20 ml hexane were added during stirring. The yellow crystals formed were filtered and washed with hexane. Yield 190 mg (97%). (Found: C, 65.4; H, 5.6; P, 8.9; Rh, 14.8. Mol.wt., 720±30. $C_{39}H_{33}O_3P_2Rh$ calcd.: C, 65.5; H, 4.62; P, 8.68; Rh, 14.4%. Mol.wt., 714.)

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